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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) Internati	nal Patent	Classification	5	:
C08J 5/1		3/38		

A1

(11) International Publication Number:

WO 93/23459

C08L 33/24

(43) International Publication Date:

25 November 1993 (25.11.93)

(21) International Application Number:

PCT/US93/02051

(22) International Filing Date:

9 March 1993 (09.03.93)

(30) Priority data:

07/883,830

15 May 1992 (15.05.92)

US

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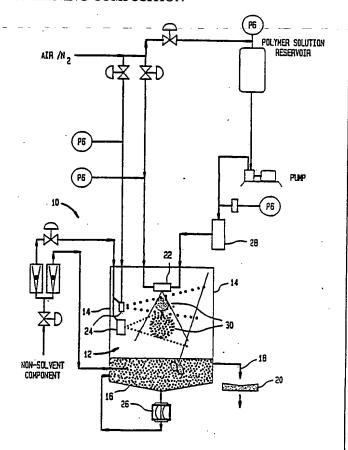
(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

With international search report.

(54) Title: SELF-LUBRICATING POLYBENZIMIDAZOLE-CONTAINING COMPOSITION

(57) Abstract

A composition, containing a polymeric blend and internal lubricants, wherein said blend consists essentially of from about 60 to about 100 weight percent of polybenzimidazole and from about 0 to about 40 weight percent of poly(aryletherketone), and said lubricants consist essentially of graphite and boron nitride in a weight ratio of about 1:10 to about 10:1, respectively. The polymer solution is pumped from a reservoir through a filtering system (28) before feeding it through the first inlet of nozzles (22). To aid atomization, a gas such as air or nitrogen is fed into a second inlet of the nozzles (22). An atomization reactor system is utilized to form the highly porous particles of the invention. The reactor system (10) has a cylindrical vessel (12) with upstanding side walls (14) and a coneshaped bottom (16) with an outlet (18) equipped with a particle separation system (20). Many nozzles are contained within the reactor. A recirculation pump (26) maintains suspension of the rounded particles in the non-solvent solution prior to discharging through outlet (18).



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SELF-LUBRICATING POLYBENZIMIDAZOLE-CONTAINING COMPOSITION

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FIELD OF THE INVENTION

The present invention is directed to a polybenzimidazole-containing composition containing internal lubricants and processes for the preparation of the composition. The composition is useful for forming low friction, shaped articles including bearings, bearing sleeves, rings, etc.

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BACKGROUND OF THE INVENTION

Polybenzimidazoles and poly(aryletherketones) are polymers of high thermal stability and excellent resistance to oxidative and hydrolytic degradation. Polybenzimidazol and poly(aryletherketone) blends are known for their excellent mechanical, thermal and chemical resistance-properties. U.S. Patent No. 4,912,176 to Alvarez et al., herein incorporated by reference in its entirety, discloses blends of polybenzimidazole and polyaryleneketones and sintered articles produced therefrom. Alvarez '176 further discloses that polybenzimidazole/ poly(aryletherketones) may be formed into article such as gaskets, seals, valve seats and O-ring backups.

However, these polybenzimidazole/poly(aryletherketone) articles are not highly durable and wear resistant when

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subjected to friction environments. These articles tend to over heat and degrade under low friction conditions after short periods of time. It is desirable to produce a polybenzimidazole-containing composition that exhibit good mechanical and physical properties as well as wear resistance in frictional environments.

BRIEF DESCRIPTION OF THE DRAWINGS

While the specification concludes with claims

10 particularly pointing out and distinctly claiming the
present invention, the present invention will be better
understood from the following description and figures in
which:

15 FIG. 1 is a schematic view in elevation of an atomization reactor utilized to form particles of the invention; and

FIG. 2 is a front view in elevation of a heat treating shell system utilized for shaped articles of the invention.

SUMMARY OF THE INVENTION

The present invention is directed to a polymeric invention containing internal lubricants being suitable for forming a low friction, shaped article containing from about 65 to about 85 weight percent of a polymeric blend and from about 15 to about 35 weight percent of internal lubricants, wherein said blend consists essentially of from about 60 to about 100 weight percent of an aromatic polybenzimidazole and from about 0 to about 40 weight percent of poly(aryletherketone), and said lubricants

consist essentially of graphite and boron nitride in a weight ratio f about 1:10 to about 10:1, respectively.

DETAILED DESCRIPTION OF THE INVENTION

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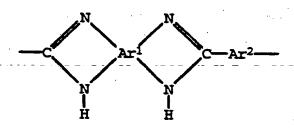
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The Polymeric Blend

Generally, the aromatic polybenzimidazole useful in the present composition may be any polybenzimidazole resins known to those skilled in the art. Typical polymers of this class and their preparation are more fully described in U.S. Patent No. 2,895,946; U.S. Patent No. Re. 26,065; and the Journal of Polymer Science, Vol. 50, pages 511-539 (1961), which are herein incorporated by reference in their entirety. These polybenzimidazoles consist essentially of recurring units of the Formula I:

Formula I is:

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wherein Ar^1 represents a tetravalent aromatic moiety having the formula:

wherein R^1 is O, SO_2 , CH=CH, $C(CF_3)_2$ or $(CH_2)_x$ and wherein x 30 is an integer of from 1 to 4; and Ar^2 represents a divalent aromatic moiety having the formula:

wherein R^2 is O. SO_2 , CH=CH, $C(CF_3)_2$ or $(CH_2)_x$ and wherein x is an integer of from 1 to 4.

A useful polybenzimidazole for use in the present invention is poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole.

The preferred polybenzimidazole is Celazole U-60 from Hoechst Celanese Corporation.

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Poly(aryletherketones) and methods of preparation are well known to those skilled in the art. Suitable methods for preparing the poly(aryletherketones) of the invention are disclosed in U.S. Patent Nos. 3,441,538; 3,442,857; 3,516,966; and 3,652,409 all of which are herein incorporated by reference in their entirety.

The preferred poly(aryletherketone) is polyetheretherketone (PEEK) having recurring units of the formula:

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red polyetheretherketone powder is available from ICI as Victrex 150 PFTH and has a molecular weight of about 150.

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Generally, the polybenzimidazole/poly(aryletherketone) blend useful for forming the self-lubricating composition of the present invention contains from about 35 to about 100 weight percent of an aromatic polybenzimidazole and from about 0 to about 65 weight percent poly(aryletherketone). Typically, the blend will contain about 40 to about 95 weight percent polybenzimidazole and from about 5 to about 60 weight percent of poly(aryletherketone), based on the total weight of the blend.

Polymeric Blend Solution Preparation

The polymeric blend of the invention are generally formed from a polymeric solution (i.e., dope). The polymeric solution may be prepared by separately or jointly dissolving a polybenzimidazole and poly(arlyetherketone) resin in a suitable solvent. While any substance that will dissolve both resins is suitable for forming the solution of the invention, typical solvents are N,N'-dimethylacetamide, N,N'-dimethylformamide, dimethylsulfoxide, and N-methyl-2-pyrrolidone, formic acid,

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acetic acid, sulfuric acid, polyphosphoric acid, and methanesulfonic acid. Particularly, the preferred solvent is N,N'-dimethylacetamide (DMAc) having a concentration of from approximately 90 to approximately 100 percent, and preferably approximately 99 percent by weight.

Methods of dissolving the polymers in a variety of solvents are known to those skilled in the art. suitable method requires drying the starting polymers to a moisture level of about 2 weight percent in a vacuum oven at a temperature of about 100°C to about 160°C for about 10 to about 16 hours. Preferred conditions for dissolving the polymers comprise heating the mixture of polymer and solvent in a stainless steel reactor at a pressure of from about 2 to about 7 atmospheres for about 2 hours at a temperature of from about 25° to about 125°C. The resulting solution is preferably filtered to remove any undissolved polymer prior to being processed. Optionally, the two polymers may be individually dissolved in the solvent and subsequently mixed together in the desired proportions.

The solution or dope of the polymeric resin dissolved in a suitable solvent generally contains from about 5 to about 35 percent by weight of polymer solids, based on the total weight of the solution. Typically, however, the solution will contain from about 10 to about 30 percent by weight of solids, and preferably, the solution will contain about 25 percent by weight of polymer solids, based on the total weight of the solution.

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The Lubricants

The lubricants useful in the polym ric composition of the present invention include graphit crystals and fibers, boron nitride, and mixtures thereof. Preferably, the 5 lubricants contained in the composition will graphite crystals (i.e, particles), graphite fibers and boron nitride powder. The preferred particulate (i.e., powder) graphite lubricants are those distributed by Superior Graphite Co. under the names Crystalline Graphite, High Purity Grade 4939™, Crystalline Graphite Grade 4735™, 10 and Crystalline Graphite 4935 ... The preferred graphite fibers which also act as a filler or reinforcement agent are Magnamite Fibers 1810AS distributed by Hercules. The boron nitride useful in the composition is distributed by Union Carbide under the trade name UCAR Boron Nitride 15 Powder Grade HCPTM.

The Coupling Agent

A coupling agent is utilized bind the components of 20 the polymeric composition together. The agent may contain, active ingredient, neoalkenolate-tris(3amino) phenylatozirconium (VI). The preferred coupling agent is NZ09 distributed by Petro Chemicals. A mixture of about 90 wt% of NZ09 and about 10 wt% of PBI particles are blended together to form an NZ09 Master Batch.

The Polymeric Composition

The polymeric composition of the invention which is suitable for forming a low friction shaped article contains from about 25 to about 35 weight percent polybenzimidazole, from about 40 to about 50 weight percent

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of poly(aryletherketone), from about 10 to about 15 weight percent of graphite fibers, from about 5 to about 15 weight percent of graphite powder, from about 1 to about 5 weight percent of boron nitride, and from about 1 to about 5 weight percent of a coupling agent, based on the total Preferably, the polymeric weight of the composition. composition will contain about 27.5 weight percent of of percent polybenzimidazole, about 40.5 weight poly(aryletherketone), about 12.25 weight percent of graphite fibers, about 10.2 weight percent of graphite particles, about 3.0 weight percent of boron nitride, and about 2.55 weight percent of coupling agent.

After preparation of the polymeric solution, the filler and lubricants are thoroughly mixed therewith to form a polymer-lubricant slurry. Initially, the lubricants (i.e., graphite and boron nitride) are dry blended in suitable proportions and added to the polymeric solution to form a slurry. Adding the lubricants to the polymeric solution is believed to cause in polymer encapsulation of the lubricants which results in shaped articles exhibiting improved strength and modulus.

particles of the polymeric composition of the invention may be formed from the slurry by precipitation and spray-atomization/quenching of polymer-lubricant slurry.

Generally, the method of forming particles by grecipitation requires the combination of the slurry and a non-solvent. The slurry, containing the polymeric solution

and lubricants may be added to a suitable non-solvent (i.e., direct precipitation) or the non-solvent may be added to the slurry (i.e., reverse precipitation). In either case the components are mixed together while undergoing constant shearing, and an excess amount of non-solvent is utilized to precipitate all the particles out of the polymeric solution.

10 An atomization reactor system, as illustrated in FIG. 1, is utilized to form the highly porous particles of the The reactor system (10) has a cylindrical vessel (12) with upstanding side walls (14) and a coneshaped bottom (16) with an outlet (18) equipped with a 15 particle separation system (20). Typical reactor dimensions are about 36 inches in diameter by about 37 inches in height. A plurality of nozzles are contained within the reactor. The first set of nozzles (22), slidably attached to the top-center of the reactor, are utilized to atomize the resin solution downwardly into the 20 reactor. A second set of nozzles (24), equaling about four times the quantity of the first nozzle set, separated into an equal number of rows (i.e. four), equally spaced and attached to the reactor side walls at positions well below the first nozzle set, are utilized to atomize the non-25 solvent component in a direction perpendicular to that of the resin solution and horizontally into the reactor to create an aggregation zone. A recirculation pump (26) is positioned in the bottom of the reactor to maintain suspension of the rounded particles in the non-solvent 30 solution prior to discharging through outlet (18).

The atomization nozzles, manufactured by Spraying Systems of Wheaton, Illinois, produce a wide-angle rounded spray pattern using a No. 1 spray set-up containing Fluid Cap 2050 and Air Cap 64. Under normal operation at 60 psi the nozzles are capable of delivering 0.79 gallons of liquid per hour at a spray angle of about 18 degrees. The polymer solution is pumped from a reservoir through a filtering system (28) to remove undissolved resin before feeding it through the first inlet of nozzles (22). To aid atomization, a gas such as air or nitrogen is fed into a second inlet of the nozzles (22) as is typical of gasoperated atomization nozzles. These nozzles (22) are suspended along the upper-vertical axis of the reactor in such a way as to spray fine droplets of the resin solution down into the reactor. The non-solvent component (e.g. water or alcohol) is fed into a first inlet of each of the second set of nozzles (24) while a compressed gas such as air or nitrogen is fed into a second inlet of each second nozzle (24) to aid in atomization. When the non-solvent component is water, from about 1 to about 2 weight percent DMAc is sometimes added to dilute the solvent. solvent adequately diluted the precipitated is not particles will often remain soft and may agglomerate.

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During operation of the reactor, the polymer solution aerosol jet is discharged from the first set of nozzles (22) downwardly into the atomized atmosphere of the non-solvent component, which is discharging horizontally into the agglomeration (i.e. reaction) zone (30) in the form of an aerosol jet from the second set of nozzles (24) to form highly porous particles. An initial quantity of non-

solvent component, e.g. water, is accumulated in the reactor bottom to maintain suspension of the highly porous particles as they are formed, as well as to compl te any residual precipitation from solution that may be necessary. Typically, the reactor is operated at atmospheric pressure, but other pressures are possible. The contents in the bottom of the reactor (i.e., polymeric particles suspended in the non-solvent component) are constantly recirculated to aid in suspension of the particles before discharging 10 through outlet (18). To separate the suspended particles from the solvent - non-solvent solution, the outlet of th reactor is typically equipped with a separation system The separation system can comprise any of several methods known in the art including vacuum filtration or 15 centrifugation. For example, the particles can be collected on the filter and washed to remove residual solvent and non-solvent components, or the slurry can b centrifuged to produce a wet cake which can be washed and The wet cake that results after filtration or centrifugation must be dried to a controlled or defined 20 moisture_content that assures adequate cold compactibility. One of several approaches can be adopted: 1- wet cake powder can be dried to lower non-solvent content (<7 wt%) and humidified to the desired moisture content (7-12 wt%); or 2- the wet cake powder can be dried directly to the 25 desired moisture content (when the non-solvent is water). Thereafter, the dried, free-flowing highly porous particles can be milled and screened if so desired to produce submicron particles.

In both of the methods described hereinbefore, th

miscibility of the solvent and non-solvent causes precipitation of the polymer particles which are collected, washed to remove residual solvent and dried. The non-solvent may be any solution which in miscible with the solvent but not the resin of the polymeric solution. Typical non-solvents useful with the solvents referenced hereinbefore include water and C₁ to C₄ aliphatic alcohols, i.e., methanol, etc. The preferred non-solvent is water.

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In the case of compositions containing higher concentrations of poly(aryletherketones), the composition may be extruded and injection molded into self-lubricating, shaped articles. In the case of compositions containing lower concentrations of poly(aryletherketones), the composition may be compressed into a densified, self-lubricating, shaped article utilizing the direct forming method and apparatus illustrated in FIG. 2.

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Referring to FIG. 2, the polymeric composition (50) is placed into the molding means (52) followed by placing end plates (54) on each side of the composition. Next, the flowable resilient, compactible material (56), e.g., Graphite 9400TM from Superior Graphite, is placed in the molding means over the end plates in such a way that the composition is separated from the resilient, compactible material. Optionally, additional end plates can be placed over the resilient, compactible material to prevent any loss of material from the molding means. Thereafter, the

molding means (50) containing the aforementioned components is placed into a clamping means comprising slidingly opposed base plates, consisting of a first base plate having a raised surface (58) and second base plate having a raised surface (58) connected by locking means (60) in such a way that the base plates raised surfaces slidably contact the resilient compactible material or optional end plates. A uniaxial pressure placed against the base plates to force the raised surfaces to slide inward and cause a pressure transmission to the polymeric material. The pressure is held constant by locking means (62), and the heat treating shell system is placed into an oven containing an air or inert gas atmosphere such as nitrogen, argon, etc., at the desired temperature for the desired Upon completion of the heat treating step, the time. pressure of the molding means is reduce to atmospheric conditions, the clamping means is disassembled, the molding means withdrawn therefrom, and the heat treated, shaped polymeric article is removed. During the process, the polymeric composition is compacted by -transmission from the pressurizing means to the clamping means to the resilient, compactible material to the polymeric composition by way of the molding means. process utilizes pressures ranging from approximately 2 to approximately 60 ksi, heat treating temperatures ranging from approximately 200° to approximately 700° C., and heat treating times ranging from approximately 5 to 10 hours.

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Shaped articles such as bearings, bearing sleeves, 30 rings and other self-lubricating article which exhibit good mechanical and physical properties may be formed from the

composition of the present invention.

The following examples are general illustrations of preparing the polymeric composition of the invention. They are provided for purposes of exemplification only as should be appreciated from the foregoing discussion.

EXAMPLE 1

Dry Blend of PBI/PEEK and Boron Nitride-Graphite

10 <u>Composition</u>

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To prepare a dry blend of a polymeric composition containing PBI, boron nitride and graphite, the following components were utilized:

378 gm of Celazole® PBI powder, 100 mesh;
611.7 gm of PEEK;
168.4 gm of Graphite Fibers;
140.2 gm of Graphite 4939;
42 gm of Boron Nitride powder; and
34.4 gm of NZ09 Master Batch

The resins, i.e., PBI and PEEK, were dried in a dehumidifier overnight at a temperature of 390°F. To a Henschel mixer operated at moderate speed, the lubricants and filler were added and sheared for about 5 minutes; thereafter, the resin powders were slowly added to the mixer and sheared an additional 10 minutes after. Finally, the coupling agent (NZ09 Master Batch) was added to the mixer, and the blend was sheared for an additional 5 minutes. The blend was extruded utilizing a multizone, twin screw extruder operated at of 350 rpm, a feeder

temperature of 175°C, a torque of from 27 to 70%, zone temperatures of from 425 to 470 C; the feed rate of the blend was from about 15 to 52 lbs/hr to form pellets. The pellets were dried at a temperature of 325 to 390°F in a forced air descant oven. Thereafter, the pellets were fed into an injection mold operated at conventional pressure, velocity and cycle time settings, a nozzle temperature setting of 750° to 825°F, and barrel temperature setting of 800° to 825°F to form disk for mechanical and tribological analyses.

COMPARATIVE EXAMPLE 2

Dry Blend of PBI and 5 wt% Graphite Composition

A sufficient quantity of PBI resin, 100 mesh was dehumidified overnight at 390°F, 431 gm of this resin and 22.68 gm of Graphite 4939 were slowly added to a Henschel mixer operated at a moderate speed. Upon completion of the addition, the blend was sheared for 10 minutes. The dry blend was compression molded utilizing the apparatus in FIG. 2 at a temperature of 890°F and a pressure of 40 tons for 4 hours to form disks. After cooling, the disks were removed from the mold for mechanical and tribological analyses.

25 COMPARATIVE EXAMPLE 3

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Dry Blend of PBI and 10 wt% Graphite Composition

The procedures of Comparative Example 2 were utilized to prepare a dry blend containing 408.6 gm of PBI resin, 100 mesh and 45.4 gm of Graphite 4939. The blend was ball milled for 2 hours and compressed into disks utilizing the procedure and apparatus of Comparative Example 2.

Mechanical and tribological analyses were performed on the disks.

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EXAMPLE 4

Precipitation of PBI and Boron Nitride-Graphite Composition

solution (standard dope) Utilizing a 26.5 wt% PBI maintained at 50°C, a 7.5 wt% PBI solution was prepared by mixing 85 gm of DMAc and 35.5 gm of the standard dope. Boron nitride and Graphite 4939 in the amounts of 27.5 gm and 27.5 gm, respectively were mixed with the dope speed, 27.5 gm of boron nitride and graphite in a 10:1 weight ratio was added to this solution to form a slurry. 15 Waring blender containing 1000 ml of water which was agitated sufficiently to vortex the solution without adding air, the slurry was slowly poured directly into the PBI-lubricant shoulder of the vortex. precipitated out of the DMAc when contacted with the water. 20 After the solution addition was complete, additional water was added to the blender to bring the liquid level to one liter, and agitation was continued for an additional 2 to 3 min. The solution was vacuum filtered through a No. 4 The precipitate was added to the blended 25 Whatman filter. containing 1000 ml of hot distilled water and agitated for 3 to 5 minutes to remove any excess solvent. After this procedure was performed three times, the precipitate was vacuum filtered and dried in a vacuum oven overnight at 150°C. The dried polymeric composition was compressed into 30 disks utilizing the apparatus and conditions of Comparative

> Mechanical and tribological analyses were Example 2. performed on the disks.

COMPARATIVE EXAMPLE 5

Precipitation of PBI and Boron Nitride Composition

Utilizing 26.5 wt% PBI solution (standard dope) maintained at 50°C, a 7.5 wt% PBI solution was prepared by mixing 85 gm of DMAc and 35.5 gm of the standard dope. Boron nitride in the amount of 27.5 gm was mixed with the solution to form a slurry. A Waring blender containing 500 ml of distilled water was agitated a sufficient speed to vortex the water without the addition of large amounts of air and the slurry was slowly poured directly into the water on the shoulder of the vortex. PBI particles began to precipitate from the solution. Thereafter, the liquid level of the blender was brought to the 1 liter level by the addition of water and the mixture was agitated for an 20 additional 2 to 3 minutes. The mixture was poured into a Buchner funnel and filtered. The precipitate was washed in the blender with 100 ml of hot distilled water for about 3 to 5 minutes, and the water was decanted from the solids. After this procedure was repeated three times, the final wash was filtered to form a cake which was dried overnight at 150°C in a vacuum oven. The dried particles were compressed into disks utilizing the apparatus and procedure of Comparative Example 2. Mechanical and tribological analyses were performed on the disks.

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EXAMPLE 6

Spray-Atomization of PBI and Boron Nitride-Graphite Composition

To 12 wt% PBI solution containing 540 gm of PBI were added 27 gm of Graphite 49339 and 27 gm of HCP boron nitride to produce a slurry containing 5 wt% of graphite and 5 wt% boron nitride. The slurry was filtered to remove impurities and any undissolved solids. Utilizing the apparatus of Figure 1, the slurry was fed through a pumping system to the first set of nozzles at a rate of 12.4 cm3/min and a pressure of 30 psi along with nitrogen gas at 15 psi was fed to the same nozzle to atomize the slurry. Water (75,700 gm) was purged with nitrogen for 48 hours followed by the addition of 764 gm (1 wt. %) of DMAc thereto. portion of this water was utilized to provide a liquid 15 layer in the bottom of the tank, and the excess water was feed to the second set of nozzles located in the tank at a rate of 1080 cm³/min assisted by nitrogen gas at 10 psiand a pressure of 25 psi. Highly porous, rounded polymeric particles formed as a result of the operation were 20 collected from the bottom of the tank, centrifuged, washed and dried. These particles were Kady milled for 1 hour at 90°C, and thereafter directly formed into disks utilizing the apparatus and conditions of Comparative Example 2. Mechanical and tribological analyses were performed on the disks. 25

EXAMPLE 7

Spray-Atomization of PBI/PEEK and Boron Nitride-Graphite Composition

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To a 12 wtt PBI solution containing 475.0 gm of PBI was added sufficient 35 wtt PEEK solution containing 768.6 gm of PEEK to prepare a polymeric solution comprising 38/62 weight ratio of PBI to PEEK. A lubrication blend containing 176.2 gm of Graphite 4939, 211.6 gm of Magnamite Fibers 1810AS and 51.8 gm of HCP boron nitride was mixed together and added to the polymeric solution to form a slurry. The slurry was filtered and spray-atomized utilizing the apparatus and conditions of Example 6. The particles were formed into disks utilizing the apparatus and conditions of Comparative Example 2. Mechanical and tribological analyses were performed on the disks.

CLAIMS

We claim:

1. A polymeric composition containing internal 5 lubricants said composition being suitable for low friction, shaped comprising from about 65 to about 85 weight percent of a polymeric blend and from about 15 to about 35 weight percent of internal lubricants, 10 based on the total weight of the composition, wherein said blend consist essentially of from about 60 to about 100 weight percent of an aromatic polybenzimidazole and from about 0 to about 40 weight percent of poly(aryletherketone), 15 and said lubricants consist essentially of graphite and boron nitride in a weight ratio of about 1:10 to about 10:1, respectively, and wherein said lubricants are well dispersed within the polymeric blend.

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- 2. The polymeric composition according to Claim 1 wherein the aromatic polybenzimidazole is poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole.
- 25 3. The polymeric composition according to Claim 2 wherein the poly(arlyetherketone) is polyetheretherketone.
- 30 4. The polymeric composition according to Claim 3 wherein the graphite is selected from the group

consisting of graphite fibers, graphite particles and mixtures thereof.

- - A self lubricating, shaped article formed from the polymeric composition according to Claim 5.
- 20 7. A self-lubricating shaped article suitable for low__friction__applications__prepared_from_-a polymeric composition containing lubricants, said composition comprising from about 65 to about 85 weight percent of 25 polymeric blend and from about 15 to about 35 weight percent of internal lubricants, based on the total weight of the composition, wherein said blend consist essentially of from about 60 to 100 weight percent of an aromatic polybenzimidazole and from about 0 to about 40 30 weight percent of poly(aryletherketone), and said

lubricants consist essentially of graphite and boron nitride in a w ight ratio of about 1:10 to about 10:1, respectively, and wherein said lubricants are well dispersed within the polymeric blend.

8. The polymeric composition according to Claim 1 wherein the aromatic polybenzimidazole is poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole.

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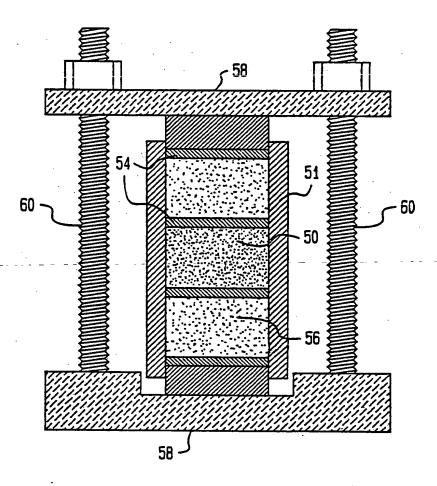
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- 9. The shaped article according to Claim 8 wherein the poly(aryletherketone) is polyetheretherketone.
- A self lubricating, shaped article containing 15 10. internal lubricants said article being useful for forming a low friction applications, comprising from about 25 to about 35 weight percent of polybenzimidazole, from about 40 to about 50 20 weight percent of poly(aryletherketone), from about 10 to about 15 weight percent of graphite fibers, from about 5 to about 15 weight percent of graphite particles, from about 1 to about 5 weight percent of boron nitride, and from about 25 1 to about 5 weight percent of a coupling agent, based on the total weight of the composition.
- 11. The self-lubricating article according to Claim 19 selected from the group consisting of 30 bearings, bearing sleeves and rings.

12. Lubricated polymeric composition comprising a high temperature aromatic polymer intimately combined with a lubricating system which consists essentially of graphite and boron nitride in a weight ratio of 10:1 to 1:10.

FIG. 1 POLYMER SOLUTION RESERVOIR AIR /N₂ 28 30 24 12 -NON-SOLVENT COMPONENT 26

FIG. 2



A. CLASSIFICATION OF SUBJECT MATTER IPC(5) :C08J 5/10; C08K 3/38; CO8L 33/24 US CL :521/184; 524/404; 525/435 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 521/184; 524/404; 525/435 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)						
C. DOC	UMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where app	ropriate, of the relevant passages	Relevant to claim No.			
X,P	US, A, 5,139,863 (ALVAREZ ET AL.) 18 AUGUST 1992 See 1-12 entire document.					
X	US, A, 4,810,730 (LETINSKI ET AL) 07 MARCH 1989 See 1-12 entire document.					
X	US, A, 4,738,999 (BLENNER ET AL.) 19 APRIL 1988 See 1-12 entire document.					
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Fort	ner documents are listed in the continuation of Box C	See patent family annex.				
"A" do	recial categories of cited documents: coment defining the general state of the art which is not considered be part of particular relevance riter document published on or after the interestional filing date ocument which may throw doubts on priority claim(s) or which is ted to establish the publication date of another citation or other ocial reason (as specified) comment referring to an oral disclosure, use, exhibition or other ones	"Y" document published after the instead and not in conflict with the application principle or theory underlying the inv "X" document of particular relevance; the considered novel or cannot be considered to reconstant be considered to involve an inventive considered to involve an inventive combined with one or more other and being obvious to a person stilled in the document member of the same parameters."	ation but cited to understand the custion as claimed invention cannot be trud to involve an inventive step as claimed invention cannot be a step when the document is a document, such combination be art			
	Date of the actual completion of the internati nal search Date of mailing of the international search report					
04 MAY 1993 03 AUG 1998						
Commissi Box PCT Washingto	mailing address of the ISA/US oner of Patents and Trademarks on, D.C. 20231 No. NOT APPLICABLE	A 11 1 1 CC	of ph			